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(54) LIQUEFACTION OF GASES  
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(21) 43493/85 (22) 12.6.85 (24) 12.6.84  
(31) 21353/84 (32) 12.6.84 (33) IT  
(43) 19.12.85  
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(74) PO  
(57) Claim

1. Process for the cooling and the liquefaction of gases, or of gas mixtures, of low boiling point, characterized in that it envisages three closed-loop refrigerating cycles in series using three different refrigerating fluids, of which one is a main or primary, multicomponent, fluid; one is a secondary, multicomponent, fluid; one is a tertiary, multicomponent or pure single-component, fluid; the gas to be liquefied being first at least partly precooled by the tertiary fluid, then liquefied by the secondary fluid, and finally supercooled by the primary fluid, which primary fluid is cooled and totally or partly condensed by the secondary fluid, which in its turn is cooled and totally condensed by the tertiary fluid, which effects also the pre-cooling of the primary fluid.

AUSTRALIA

*Patents Act*

# COMPLETE SPECIFICATION

(ORIGINAL)

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Complete Specification for the invention entitled:

"PROCESS FOR THE COOLING AND LIQUEFACTION OF GASES WITH LOW BOILING  
POINT"

The following statement is a full description of this invention, including the best method of performing it known to  
applicant(s):

The object of the present invention is a process for the cooling and liquefaction of a gas with low boiling point, such as e.g. natural gases, or of any gas mixtures wherein at least a component has a low boiling point.

Processes for such applications, of the so-called "in series (cascade)" type are known, wherein the fluid to be cooled is gradually liquefied by means of successive heat exchanges with a plurality of refrigerating fluids with decreasing boiling temperatures.

10       The drawback of such processes is that a great number of heat exchangers are necessary, and the same is true for the rotary machines and the other equipment pieces.

This increases the cost of the plant, and at the same time reduces the reliability thereof. Moreover, the nature of refrigerating fluids, almost always pure or nearly pure compounds, produces flat, stepped heating curves, which do not allow the cooling curve of the gas to be cooled which has a more or less sloping continuous shape, to be complied with.

20       This determines a relatively low yield of the cooling cycle and an energy loss.

Liquefaction processes are also known, which occur by heat exchange with refrigerating multicomponent fluids undergoing a total or partial condensation, which hence produces an amount of liquid which, on evaporating in countercurrent to the fluid to be cooled, follows closely the cooling curve thereof, at least in its most important portions. In this case it is also possible to use one single compressor, with a notable simplifying of the plant.

30       Although it may appear as being an advantage,

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in the case of the liquefaction of natural gas the presently economically suitable size of an industrial liquefaction line is such that a single compressor results of a greater capacity than those up to date currently used in the industrial practice. Therefore, processes with mixed refrigerating fluid, as indicated, have been used, but using a multicomponent or pure auxiliary refrigerating fluid to the purpose of pre-cooling, in the same equipment or separately, the natural gas and the main refrigerating fluid. In this case, the closed refrigerating cycles are two, and each one of them uses a separate compressor. The yield of this type of cycles is even greater, in that the main fluid can fit well to the cooling curve of natural gas within its temperature range.

This however presupposes that the main refrigerating fluid evaporates always in the presence of its vapour phase, which presupposes a perfect distribution of the phases of the refrigerating fluid from one exchanger end to the other one, without any separations of the phases. This is made possible by the use of the exchangers of the coiled type, i.e. with a tube nest made from tubes of malleable type wound to form a coil around a cylindrical core.

Although exchangers of such a type are available with very high reliability and efficiency characteristics from the present art, their cost has remained very high; moreover, also their weight and overall dimensions are notably high and constitute further drawbacks.

A process has been found by us which allows to associate an optimum energetic efficiency and a relatively low installation cost, at the same time overcoming the hereinabove described

drawbacks.

The process being the object of the present invention envisages three closed-loop refrigerating cycles in series using three different refrigerating fluids, of which one is a main or primary, multicomponent, fluid; one is a secondary, multicomponent, fluid; one is a tertiary, multicomponent or pure single-component, fluid; the gas to be liquefied being first at least partly pre-cooled by the tertiary fluid, then liquefied by the secondary fluid, and finally supercooled by the primary fluid, which primary fluid is cooled and totally or partly condensed by the secondary fluid, which in its turn is cooled and totally condensed by the tertiary fluid, which effects also the pre-cooling of the primary fluid.

More particularly, in the first refrigerating cycle there may be envisaged for the primary refrigerating fluid at least a compression in the gaseous state, the pre-cooling by heat exchange with the tertiary fluid, the cooling and the total or partial condensation by heat exchange with the secondary fluid, a possible expansion in a valve, the separation of the liquid and vapour phases formed, the condensation, the supercooling, the expansion and the at least partial evaporation of the vapour phase before it to be admixed to the same liquid phase previously super-cooled and expanded to the same evaporation pressure as of the vapour phase, the so formed mixture being evaporated by heat exchange in countercurrent both with the liquefied gas to be supercooled, and with the liquid and vapour phases, and possibly superheated before being recompressed.

The fact that the primary cycle is only intended for the supercooling of the liquefied gas and the use thereof

within a temperature range narrower and shifted towards the low temperatures, as well as on a reduced heat load, in that the condensation of the gas to be liquefied is secured by the secondary refrigerating liquid, reduce to a notable extent its main drawback, i.e., the need of an expensive coiled exchanger.

Moreover, according to what has been previously mentioned, the pressure of condensation of the primary fluid may be increased above the needed value for obtaining the necessary partial condensation by the minimum temperature of the secondary fluid, so as to achieve the total condensation at a temperature even higher than the minimum temperature of the secondary fluid. The purpose of such a further compression is of transferring frigorific work from the secondary circuit to the primary circuit. The same purpose has the possible superheating of the primary fluid before the compression thereof, it being possible such superheating to be carried out against the cooling of a portion of condensed secondary fluid.

The interest in such a transfer resides in that it is often advantageous, or necessary, in the industrial practice, to use in the same plant compressors of nearly equal power, consequently driven by identical driving units.

The first refrigerating cycle may also be varied by envisaging for the primary refrigerating fluid after a compression in the gaseous state, the pre-cooling at least partly by means of the heat exchange with the tertiary fluid, the cooling and the total condensation by means of heat exchange with the secondary fluid, a supercooling followed by a partition into at least two streams, said streams being first expanded, the first one to a pressure

low enough to allow a further cooling before the evaporation, the other stream(s) to higher pressures than the preceding one, then evaporated by countercurrent heat exchange both with the liquefied gas to be supercooled, and with their own liquid to be supercooled, and finally possibly superheated before being recompressed and combined with each other.

The possible superheating of the two streams may be carried out by supercooling a portion of the secondary refrigerating fluid already condensed by the tertiary fluid.

10        The recompression, e.g., in the case of two streams, can be effected by compressing the low-pressure portion up to the pressure of the higher-pressure portion, then mixing it with the higher-pressure portion, after having possibly recovered the residual refrigerating units therefrom, e.g. by pre-cooling a portion of the same primary refrigerating fluid after the compression, and compressing to the end pressure the mixture formed. All low-temperature heat exchanges of the primary fluid as described can be accomplished, without any drawbacks, with plate fin heat exchangers.

20        In the second refrigerating cycle for the secondary refrigerating fluid there may be provided at least a compression in the gaseous state, the cooling and total condensation by heat exchange with the tertiary fluid, the supercooling itself, a partition into at least two streams, said streams being first expanded, the first under low pressure, the other stream(s) under different pressures higher than the preceding one, then evaporated by countercurrent heat exchange both with the gas being liquefied, and with the primary fluid, and with the same



secondary refrigerating fluid which is supercooled, before being recompressed and combined with each other to yield a single stream.

In the case of two streams, the recompression and the recombining into a single stream may be carried out by compressing the lower-pressure stream by means of a compressor with a side intake for the higher-pressure stream.

10 The liquefaction of the gas and of the primary fluid may be carried out in a single exchanger, or in a plurality of heat exchange bodies in parallel, wherein all entering and leaving fluids are single-phase fluids. It might be e.g. of the so-called plate-fin type.

Due to monophasic character of all entering fluids, any problems of uniform distribution of phases are overcome.

20 A modification to the second refrigerating cycle may be done by envisaging for the secondary refrigerating fluid, after its compression in the gaseous state, the cooling and the total condensation by heat exchange with the tertiary fluid, a first partition into two streams, said two streams being supercooled, the first one by heat exchange with the primary fluid, the other one by heat exchange with the same secondary refrigerating fluid, and the recombination thereof, a second partition into at least two streams, said streams being first expanded, the first one under low pressure, the other stream(s) under different pressures higher than the preceding one, then evaporated by countercurrent heat exchange both with the gas to be liquefied, and with the primary refrigerating fluid and with a portion of the same secondary refrigerating fluid which is supercooled, before being  
30 recompressed and recombined with each other.

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Possibly, the higher-pressure stream of the secondary fluid may be superheated, before being recompressed, by using the refrigerating units thereof to the purpose of e.g. pre-cooling a portion of the gas to be liquefied.

The tertiary refrigerating fluid, as it has hereinabove stated, may be a pure component, in which case the tertiary circuit shall be constituted by a conventional refrigerating cycle using propane, propene, ammonia, Feron\* (trade mark) or other gases, and in general of the type with 2, 3 or 4 steps, i.e., evaporation temperature levels, or it may also be a mixture of 2 or more gases.

When the tertiary refrigerating fluid is of the multi-component type, in the tertiary refrigerating cycle there may be envisaged for said refrigerating fluid a compression in the gaseous state, a cooling and a total condensation by heat exchange with an external refrigerating source, such as e.g. atmospheric air or sea water, a super-cooling and a partition into a plurality of streams, which are evaporated under different pressures, in such a way they supplying the refrigerating units necessary both for their own supercooling, and for the condensation of the secondary fluid, and for the pre-cooling of at least a portion of the gas to be liquefied.

According to the features of the present invention, the composition of the primary refrigerating fluid in the embodiment with the phase separation, evaporation under a single pressure, and re-mixing of the refrigerating fluid at a certain point of the heat exchange, may be:

|                               |   |                        |
|-------------------------------|---|------------------------|
| N <sub>2</sub>                | nitrogen                                    | from 0 to 10% by mole  |
| CH <sub>4</sub>               | methane                                     | from 40 to 70% by mole |
| C <sub>2</sub> H <sub>4</sub> | ethene and/or C <sub>2</sub> H <sub>6</sub> |                        |

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ethane

from 30 to 50% by mole

$C_3H_6$  propene and/or  $C_3H_8$

propane

from 0 to 5% by mole

In the embodiment with total condensation and evaporation under two pressures in plate-fin exchanger, the composition may be:

$N_2$  nitrogen

from 0 to 15% by mole

$CH_4$  methane

from 65 to 85% by mole

$C_2H_4$  ethene and/or  $C_2H_6$

ethane

from 5 to 35% by mole

The composition of the secondary refrigerating fluid may be:

$CH_4$  methane

from 0 to 15% by mole

$C_2H_4$  ethene and/or  $C_2H_6$

ethane

from 65 to 90% by mole

$C_3H_6$  propene and/or  $C_3H_8$

propane

from 5 to 35% by mole

The composition of the tertiary refrigerating fluid, when it is not constituted by one of the hereinabove mentioned fluids, may be:

$C_2H_4$  ethene and/or  $C_2H_6$

ethane

from 25 to 75%

$C_3H_6$  propene and/or  $C_3H_8$

propane

from 25 to 75%

The process being the object of the present invention has many advantages, among which the following may be mentioned:

- an easy adaptability of the cryogenic exchangers to the so-called plate-fin type, with evident advantages due both

to their low cost per heat exchange surface unit, and to  
the low load losses, and to their characteristics

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of modularity and compactness. This is evident for the primary cycle in the embodiment with evaporation under two pressures, in that all streams are under a practically monophasic condition, but is also valid to a certain extent for the single-pressure embodiment, due to two reasons. The first reason is that, as the size of the supercooling exchanger is much lower than that of a supercooler-liquefier of the known art, even if it had to be of the coiled type, the economic disadvantage would be thereby reduced as much. The economic reason is that by operating on a reduced size, it is possible to adopt such oversizing margins as to make it acceptable a possible reduction in efficiency due to the installation of plate-fin exchanger types.

- great flexibility, which allows a fitting to the nature and to the condition of the gas to be liquefied, at the same time maintaining an optimum thermodynamic efficiency not only for different design conditions, but also on operation, e.g., in case of a not previously foreseen change of the gas to be liquefied.

Such flexibility is mainly due to the following features of the same invention:

- adaptability of the composition, containing methane, nitrogen, ethene, ethane, propene and propane, of the primary refrigerating fluid;
- adaptability of the composition, containing methane, ethene, ethane, propene, propane, of the secondary fluid;
- evaporation pressure of the primary cycle;
- ratio of the flow rates of primary fluids evaporated under the different pressures;

- evaporation pressures of the secondary cycle;  
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- ratio of the flow rates of secondary fluid evaporated under the different pressures;
- ratio of the flow rates of liquid and vapour of primary fluid after its partial condensation by the secondary refrigerating fluid, or total condensation and subsequent expansion.

In order to make it easier the understanding of the invention, and clearer the advantages thereof, we use now the enclosed Figures 1, 2, 3 and 4, representing some preferred  
 10 embodiments thereof, which are not to be considered as being limitative of the invention itself.

#### Example 1

With reference to fig. 1, which represents the flow-sheet of the equipment for the cooling and liquefaction of a low boiling point gas such as e.g., a natural gas, wherein the powers of the three refrigerating cycles are balanced by the supercompression and the expansion of the primary fluid as hereinabove mentioned, the suitably pretreated natural gas enters the exchanger, via the pipe 1, at 35°C and under 53.4  
 20 eff.bars, with the following composition by mole:

|                         |         |
|-------------------------|---------|
| Nitrogen N <sub>2</sub> | 1.81 %  |
| methane CH <sub>4</sub> | 98.05 % |
| ethane                  | 0.14 %  |

The natural gas shall hence be cooled in the exchanger 2 by the evaporation, under decreasing pressures, of the propane as refrigerating fluid, leaving the exchanger at -30°C and under 52 eff. bars.

The pipe 3 shall lead it to the exchanger 4, wherein it shall be cooled and totally liquefied by the secondary  
 30 refrigerating fluid.

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At the outlet of the exchanger 4 we'll have hence some liquid at the temperature of  $-95^{\circ}\text{C}$  and under 50 eff. bars. The liquefied natural gas passes then, via the pipe 5, to the supercoolign in the exchanger 6 by the primary refrigerating fluid.

At the outlet of the exchanger 6 the pipe 7 shall lead it towards the storage at the temperature of  $-154^{\circ}\text{C}$  and under 48.3 eff. bars.

The primary refrigerating fluid, having the following  
10 composition by mole:

|          |                        |         |
|----------|------------------------|---------|
| Nitrogen | $\text{N}_2$           | 3.37 %  |
| methane  | $\text{CH}_4$          | 62.18 % |
| ethene   | $\text{C}_2\text{H}_4$ | 34.45 % |

leaves the exchanger 6 in the completely vapourized state at  $-98^{\circ}\text{C}$  and under 1.2 eff.bars. The pipe 8 leads it to the exchanger 9, wherein it is superheated at  $-40^{\circ}\text{C}$  and comes then, via the pipe 10, to the intake of compressor 11 under the pressure of 0.9 eff. bars.

The compressor 11, e.g. a centrifugal 6-impellers  
20 compressor, can then compress the primary gas up to 8.6 eff.bars, whilst the temperature thereof shall be increased to  $89^{\circ}\text{C}$ .

At this point, an intermediate cooling is necessary to the purpose of making it possible the compression to be continued. The pipes 12 and 13 connect hence the compressor to the exchanger 14, e.g. a sea-water-exchanger, which cools the gas down to  $40^{\circ}\text{C}$  and 8.1 eff. bars. The gas undergoes then, in an at all analogous way, a compression in the compressor 15, a cooling in the exchanger 16, a compression in the remaining  
30 portion of the compressor 15, and a cooling in the exchanger 17.  
SA

The pipe 18 leads then the primary gas at 35°C and under 38 eff. bars towards the exchanger 2, wherein the propane cycle shall cool it down to -30°C and 37.5 eff. bars.

Through the pipe 19 the gas comes finally at the exchanger 4, from which it shall stream in the completely liquefied state, and not at -95°C as all the other warm streams of this exchanger but at -76.4°C and under 37.1 eff. bars.

10 In order to obtain this, it shall be necessary to provide the exchanger 4 with a side outlet intended for the through flow of the primary refrigerating fluid. The pipe 20 therefore leads the liquid to the valve 21 which laminates it at 18.2 eff. bars, whilst the temperature, due to the evaporation of about 21.3% of the liquid reaches -95°C.

20 The liquid and vapour phases are then separated by means of the separator 22 and via the pipes 23 and 24 they enter the exchanger 6. The vapour phase leaves the top of the exchanger as condensed and supercooled at -154°C, and after lamination in the valve 25 reenters the exchanger at -160°C. While wetting the upper bundle, this fluid flows down with contemporary evaporation, up to -142°C. The said liquefied phase of the separator 22 is on the contrary supercooled in the lower bundle of the exchanger 6 down to -140°C. After having left the exchanger, it is laminated in the valve 26 at 1.5 eff. bars, and is mixed with the said vapour phase flown downward along the upper bundle, reaching the temperature of -143°C.

Wetting the lower bundle, the mixture flows downward while totally evaporating and hence supplying the refrigerating units necessary for the supercooling of the lique-



fied natural gas, as well as for the supercooling of its own, and for the condensation and the cooling of its own vapour phase.

On leaving the exchanger 6 from its bottom portion, the gas enters the pipe 8, thus closing the cycle.

The secondary refrigerating fluid, with a molar composition of:

|         |                        |        |
|---------|------------------------|--------|
| methane | $\text{CH}_4$          | 10 %   |
| ethene  | $\text{C}_2\text{H}_4$ | 80.4 % |
| propane | $\text{C}_3\text{H}_8$ | 9.6 %  |

10 is compressed to 26 eff. bars in the compressor 27, reaching the temperature of  $104^\circ\text{C}$ . The pipe 28 leads it to a de-superheater, e.g., operating with sea water, 23, which brings it back to  $35^\circ\text{C}$ . The pipe 30 leads then it to the exchanger 2, wherein it is totally condensed by propane. The liquid leaves hence the exchanger (31) at  $-30^\circ\text{C}$  and 25.1 eff. bars and is divided into two portions: one of them (32), of 23% of the stream (31) is directed to the exchanger 9, wherein it is supercooled to  $-95^\circ\text{C}$  and is then mixed again via the pipe 33 with the other portion 34, but after that this latter portion has been cooled down to  
20  $-95^\circ\text{C}$  in the exchanger 4. The so-reconstituted secondary refrigerating fluid (35) is divided again into 2 streams. The first stream (36) is laminated in the valve 37 under 2 eff. bars, thus reaching the temperature of  $-99.63^\circ\text{C}$ , to be introduced into the exchanger 4, and to leave it as completely evaporated at  $-33^\circ\text{C}$  and 1.6 eff. bars. The pipe 38 then leads it to the low-pressure intake of compressor 27. The second stream (39) in an at all analogous way is laminated in the valve 40, is evaporated in the exchanger 4 and is led to compressor 27 via the pipe 41.

30 The tertiary refrigerating cycle is a 4-step propane  
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step according to the known art, which is composed in its essential parts by a compressor 42, a condenser 43, e.g., operating with sea water, and by the separators 44, 45 and 46, as well as by the exchanger 2, which is envisaged to be in this case of the plate-fin type, but which may be substituted by an adequate number of tube-bundle exchangers of the kettle type, with the only drawback that the number is multiplied of the lamination valves analogous to those represented here with the reference characters 47, 48, 49 and 50.

10           In the present example, commercial propane is condensed at 40°C and 12.9 eff. bars and is then laminated in the already mentioned economizer separators through the valves 51, 52 and 53 respectively at 66 eff. bars and 16°C, at 2.9 eff. bars and -6°C and at 1.25 eff. bars and -22°C. Through the valve 47 the propane reaches then -32°C under 0.4 eff. bar. As propane is a pure fluid, to the practical effects it evaporates at the constant temperatures as mentioned and is thus sucked by the centrifugal compressor 42.

20           In the case herein exemplified the flow rate of natural gas to be liquefied is of 268.6 tons/hr and the computation of the process being the object of the invention in the just illustrated embodiment leads to indicative purposes to the following results:

- the primary refrigerating cycle requires the circulation of 180 tons/hr of gas which, when compressed as said from 0.9 eff. bar up to 38.4 eff. bars requires from compressors 11 and 15 a power of 25570 kW.

It is interesting to observe that the ratio of exchanged heat to the temperature average logarithmic deviation

has been kept equal to 4,120,000 kcal/hr. $^{\circ}$ C and to 780.000 kcal/hr. $^{\circ}$ C respectively for the exchangers 6 and 9.

- the secondary refrigerating cycle requires the circulation of 452 tons/hr of the mentioned gas and the compressor 27 absorbs 27240 kW. The thermal dimensioning of the exchanger 4 has been carried out on the basis of 10,150,000 kcal/hr. $^{\circ}$ C, whilst the subdivision ratio of the refrigerating fluid is of 60% evaporated under low pressure and 40% evaporated under higher pressure.

10 - the overall capacity of the propane compressor is of 1047 tons/hr and its power of 27580 kW. The exchangers are relatively small in that it is not reasonably possible to demand more than 10,000,000 kcal/hr. $^{\circ}$ C calculated.

#### Example 2

We refer to fig. 2 which represents the same flow-sheet as of fig. 1, with the exception that the tertiary cycle is a cycle with mixed refrigerating fluid, with evaporation under 3 pressures.

20 Said tertiary refrigerating cycle envisages in its essential parts a compression of the tertiary fluid in the gaseous state by means of the compressor (42), a cooling and a total condensation in 54 by means of a source of external cooling, a supercooling in 55, evaporation in (2) under three different pressures by means of the valves 56, 57 and 58, thus supplying the refrigerating effect necessary both for cooling of its own, and for the condensation of the secondary fluid and for the precooling of the gas to be liquefied, and finally the recompression of the three streams 59, 60 and 61.

The evaporation pressures are, by adapting an equi-molar mixture of ethane and propane, of 4.4, 9.1 and 16.3 eff. bars respectively for the first, the second and the third stage.

The flow rates of the refrigerating fluids 59, 60 and 61 are of respectively 475, 255 and 284 tons/hr on the 3 stages with a compressor total power of 25600 kW, thus confirming the greater efficiency of this type of cycle relatively to the cycle with pure propane, even if with 4 stages. The heat exchange curves of the refrigerating fluid fit well to the load curves, as it can be observed from the dimensioning of the exchanger 2 on the basis of 26,100,000 kcal/hr.<sup>°C</sup>, without that the minimum temperature deviation be lower than 2<sup>°C</sup> at any time.

#### Example 3

We refer now to fig. 3, which represents the same flowsheet as of fig. 2 in the modification in which the equilibrium of powers is not required, at the same time maintaining the same minimum temperatures of the three cycles as in the preceding flowsheet.

More precisely, the present flowsheet is different from the preceding one, due to the elimination of the expansion valve 21, due to the simplified exchanger 4 in that all high temperature fluids stream from it at the same temperature, and due to the use of a single compressor 11 with two intermediate cooling steps 63 and 64.

By so doing, the delivery pressure of the primary cycle is reduced down to 19.5 eff. bars, whilst, while maintaining the same overall power, the power ratios of the three compressors 11, 27 and 42 result of about 2 : 3 : 3.

#### Example 4

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Reference is now made to fig. 4, which represents a flowsheet of a different embodiment of the invention, in its modification wherein the primary cycle involves the total condensation of the refrigerating fluid and its evaporation under two pressures, with superheating of the streams sucked by the primary compressor.

The primary refrigerating fluid, having the following molar composition:

|                               |          |         |
|-------------------------------|----------|---------|
| N <sub>2</sub>                | nitrogen | 3.16 %  |
| CH <sub>4</sub>               | methane  | 69.72 % |
| C <sub>2</sub> H <sub>4</sub> | ethene   | 27.22 % |

is compressed in the compressors 11 and 15 to 35 to 35.3 bars, is cooled first in 17, then partly (18), by 54%, in the tertiary cycle with mixed refrigerating fluid, partly (65) in the exchanger 66, recovering its residual refrigerating units.

The pipes 67 and 19 deliver the primary fluid respectively streaming from the exchangers 66 and 2 into the pipe 68 and then to the exchanger 4, wherein it is liquefied by the secondary refrigerating fluid, leaving the exchanger at -83.7°C via the pipe 20, which leads it to the exchanger 6. In such an exchanger the primary fluid is supercooled, as the liquefied gas, to -154°C (69). At the outlet it is distributed into the pipes (70) and (71) respectively by 56.3% and 43.7%, and is laminated under 7.2 rel. bars and 0.43 rel bar in the valves 72 and 73. Such two streams are evaporated and heated in two different passages of the exchanger 6 up to -86.7°C. They are moreover superheated to -34°C in the exchanger 74, after which the low-pressure stream 75 is compressed in the compressor 11, de-superheated in 76 down to room temperature and

admixed to the higher-pressure stream 77, which in the mean time, by flowing through the exchanger 66 has released its residual refrigerating units.

The compressor 15, provided with an intermediate cooling in 16, brings the refrigerating fluid back to 35.3 rel. bars, closing the cycle. The overall capacity of the two compressors is of 218 tons/hr and the total power of 24940 kW.

10 The exchanger 6 is dimensioned on the basis of  $6.1 \times 10^6$  kcal/hr. $^{\circ}$ C.

The secondary cycle is at all analogous to that of the preceding embodiments and its characteristics are:

|                      |          |         |        |
|----------------------|----------|---------|--------|
| - Molar composition: | $C_1H_4$ | methane | 0.90 % |
|                      | $C_2H_4$ | ethene  | 78.5 % |
|                      | $C_3H_8$ | propane | 20.6 % |

Intake pressure: 0.80 rel. bar and 4.95 rel. bars

Delivery pressure: 16.93 rel. bars for condensation at  $35^{\circ}$ C

20 Suction ratios relatively to the total capacity respectively of 75.1% and 24.9%

Total Capacity 442.5 tons/hr, with supercooling in the exchangers 4 and 74 respectively by 66.2% and 33.8%.

Power of compressor 27: 24310kW.

✓ Dimersioning of the exchanger 4:  $12.9 \times 10^6$  kcal/h. $^{\circ}$ C.

Also the tertiary cycle with mixed refrigerating fluid is analogous to that previously illustrated and its characteristics are:

|                      |          |         |      |
|----------------------|----------|---------|------|
| - Molar composition: | $C_2H_6$ | ethane  | 50 % |
|                      | $C_3H_8$ | propane | 50 % |

|                           |               |
|---------------------------|---------------|
| Capacity of the 1st stage | 464.3 tons/hr |
| 2nd stage                 | 253.0 tons/hr |

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3rd stage                    248.4 tons/hr  
Suction pressures respectively: 4.1 rel. bars  
                                 8.5 rel. bars  
                                 16.2 rel. bars

Delivery pressure            27.9 rel. bars

Compressor power            24800 kW

Dimensioning of the exchanger 2:  $19.3 \times 10^6$  kcal/hr. $^{\circ}$ C.

10        In the preceding examples it has been supposed that  
the room temperature be of 30 $^{\circ}$ C; now, a theoretical lique-  
faction reversible cycle under the same conditions as of the  
preceding examples would require a total power of 35725 kW,  
hence the thermodynamic efficiency of the embodiment just  
illustrated is of 48.2%. If one considers that for the  
good processes of the known art such a thermodynamic  
efficiency is of generally 43% and that only for the most  
efficient of them (the Precooled Tealarc), in the  
exemplified case, a 46.4% can be achieved, the energetic  
advantage is evident of the present invention.

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The Claims defining the invention are as follows:

1. Process for the cooling and the liquefaction of gases, or of gas mixtures, of low boiling point, characterized in that it envisages three closed-loop refrigerating cycles in series using three different refrigerating fluids, of which one is a main or primary, multicomponent, fluid; one is a secondary, multicomponent, fluid; one is a tertiary, multicomponent or pure single-component, fluid; the gas to be liquefied being first at least partly precooled by the tertiary fluid, then liquefied by the secondary fluid, and finally supercooled by the primary fluid, which primary fluid is cooled and totally or partly condensed by the secondary fluid, which in its turn is cooled and totally condensed by the tertiary fluid, which effects also the pre-cooling of the primary fluid.

2. Process according to claim 1, characterized in that in the first refrigerating cycle there are envisaged for the primary refrigerating fluid at least a compression in the gaseous state, the pre-cooling by heat exchange with the tertiary fluid, the cooling and the total condensation by heat exchange with the secondary fluid, an expansion in a valve and the separation of the liquid and vapour phases formed, the condensation, the supercooling, the expansion and the at least partial evaporation of the vapour phase before it to be admixed to the same liquid phase previously supercooled and expanded to the same evaporation pressure as of the vapour phase, the so formed mixture being evaporated by heat exchange in countercurrent both with the liquefied gas to be supercooled, and with the liquid and vapour phases, and possibly superheated before being recompressed.

3. Process according to claim 1, characterized in that in the first refrigerating cycle there are envisaged for the primary refrigerating fluid at least a compression in the gaseous state, the pre-cooling by heat exchange with the tertiary fluid, the cooling and the partial condensation by heat exchange with the secondary fluid, the separation of the liquid and of the vapour phases, the condensation, the supercooling, the expansion and the at least partial evaporation of the vapour phase before it to be admixed to the same liquid phase previously supercooled and expanded to the same evaporation pressure as of the vapour phase, the so formed mixture being evaporated by heat exchange in countercurrent both with the liquified gas to be supercooled, and with the liquid and vapour phases, and possibly superheated before being recompressed.

4. Process according to claim 1, characterized in that in the first refrigerating cycle there are envisaged for the primary refrigerating fluid a compression in the gaseous state, the pre-cooling at least partly by means of heat exchange with the tertiary fluid, the cooling and the total condensation by means of heat exchange with the secondary fluid, the supercooling and the subdivision into at least two streams, said streams being first expanded, the first one to a pressure low enough to allow a further cooling before the evaporation, the other stream or the other streams to higher pressures, then being evaporated by countercurrent heat exchange both with the liquefied gas to be supercooled, and with their own liquid to be supercooled, and being finally superheated before being recompressed and combined with each other.

5. Process according to claim 2 or 3 or 4, wherein

the superheating of the streams occurs by heat exchange with a portion of the secondary refrigerating fluid previously condensed by the tertiary refrigerating fluid.

6. Process according to claim 4, wherein the divided streams are two, and the recompression thereof takes place by first compressing the low-pressure stream up to the pressure of the higher-pressure stream, then admixing it to the higher-pressure stream, after having possibly recovered the residual refrigerating units therefrom, and finally compressing the  
10 mixture formed to the end pressure.

7. Process according to claim 6, wherein the recovery of the residual refrigerating units of the higher-pressure stream occurs by pre-cooling a portion of the same primary refrigerating fluid after its compression.

8. Process according to claim 1, characterized in that in the second refrigerating cycle there are envisaged for the secondary refrigerating fluid at least a compression in the gaseous state, the cooling and the total condensation by heat exchange with the tertiary fluid, the supercooling with itself,  
20 the subdivision into at least two streams, said streams being first expanded, the first one under low pressure, the other stream(s) under high pressures, being then evaporated by countercurrent heat exchange both with the gas being liquefied, and with the primary refrigerating fluid, and with the same secondary refrigerating fluid which is supercooled, before being recompressed and combined with each other.

9. Process according to claim 1, characterized in that in the second refrigerating cycle there are envisaged for the secondary refrigerating fluid at least a compres-

sion in the gaseous state, the cooling and the total condensation by heat exchange with the tertiary fluid, a first subdivision into two streams, said two streams being supercooled, the first one by heat exchange with the primary fluid, the other one by heat exchange with the same fluid, and the recombination thereof, a second subdivision into at least two streams, said streams being first expanded, the first one under low pressure, the other stream(s) under higher pressure, being then evaporated by countercurrent heat exchange both  
10 with the gas to be liquefied, and with the primary refrigerating fluid, and with a portion of the same refrigerating fluid which is supercooled, before being recompressed and recombined with each other.

10. Process according to claim 8 or 9, wherein the highest pressure stream of the secondary refrigerating fluid, before being recompressed, is superheated to the purpose of cooling a portion of the gas to be liquefied.

11. Process according to claim 1, characterized in that in the tertiary refrigerating cycle there are envisaged  
20 for the tertiary refrigerating fluid consisting of a pure component, 2, 3 or 4 steps or evaporation temperature levels.

12. Process according to claim 1, characterized in that there are envisaged in the refrigerating cycle for the multi-component tertiary refrigerating fluid, a compression in the gaseous state, a cooling and a total condensation by heat exchange with a source of external refrigeration, a supercooling and a subdivision into a plurality of streams which are evaporated under different pressures, thus supplying the refrigerating units necessary both for their own

30 supercooling and for the condensation  
SA

tion of the secondary fluid, and for the pre-cooling of at least a portion of the gas to be liquefied.

13. Process according to claims 1 and 2 or 3 wherein the primary refrigerating fluid contains methane from 40 to 70% by mole, ethene and/or ethane from 30 to 50% by mole, nitrogen from 0 to 10% by mole, propene and/or propane from 0 to 5% by mole.

10 14. Process according to claims 1 and 4 wherein the primary refrigerating fluid contains methane from 65 to 85% by mole, nitrogen from 0 to 15% by mole, ethene and/or ethane from 5 to 35% by mole.

15. Process according to claims 1 and 8 or 9, wherein the secondary refrigerating fluid contains methane from 0 to 15% by mole, ethene and/or ethane from 65 to 90% by mole, propene and/or propane from 5 to 35% by mole.

16. Process according to claims 1 and 11, wherein the pure-component tertiary refrigerating fluid is selected among propane, propene, ammonia or Freon\*.

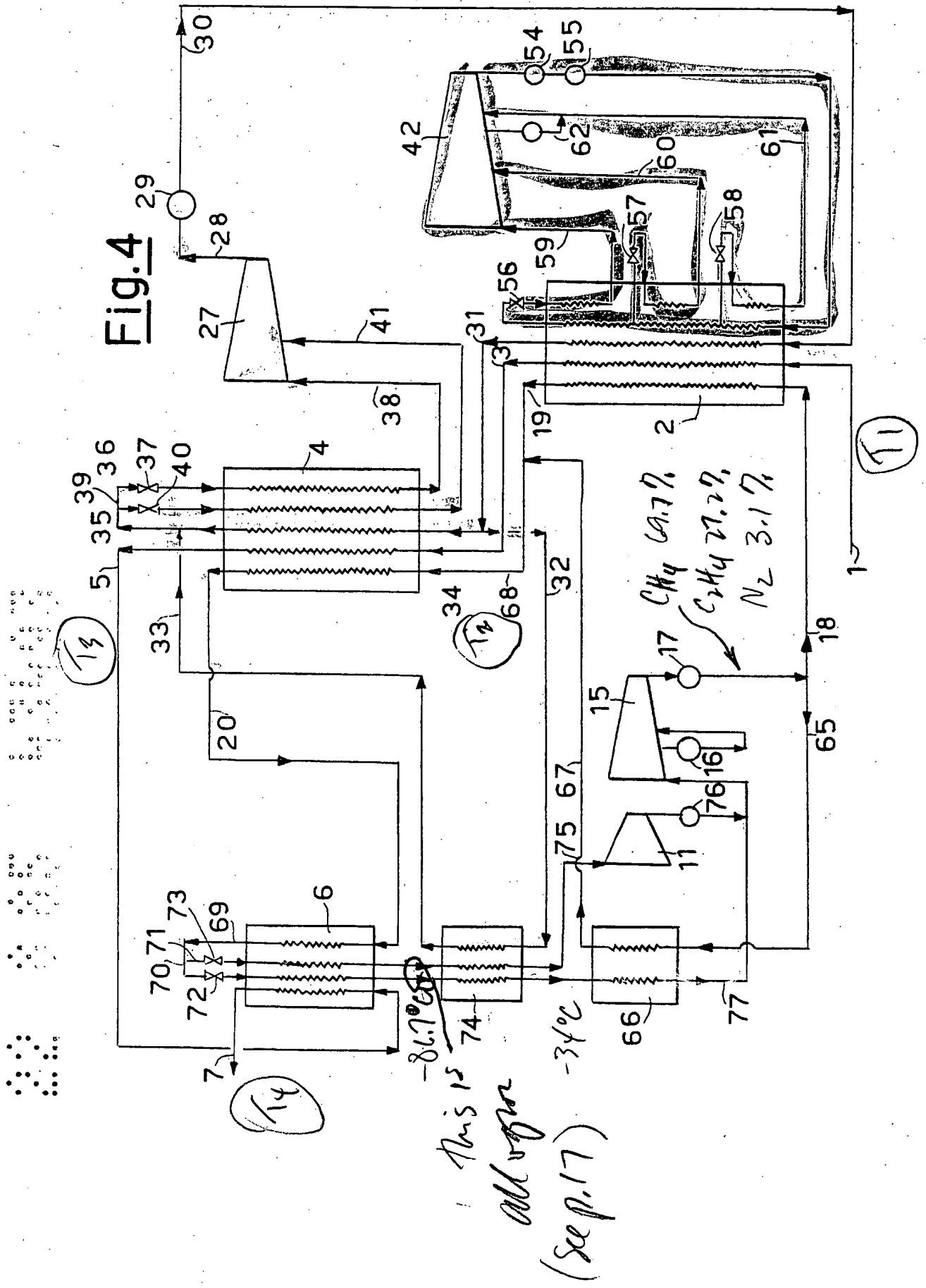
20 17. Process according to claims 1 and 12 wherein the multi-component tertiary refrigerating fluid contains ethane and/or ethane from 25 to 75% by mole, propene and/or propane from 25 to 75% by mole.

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**Fig. 4**



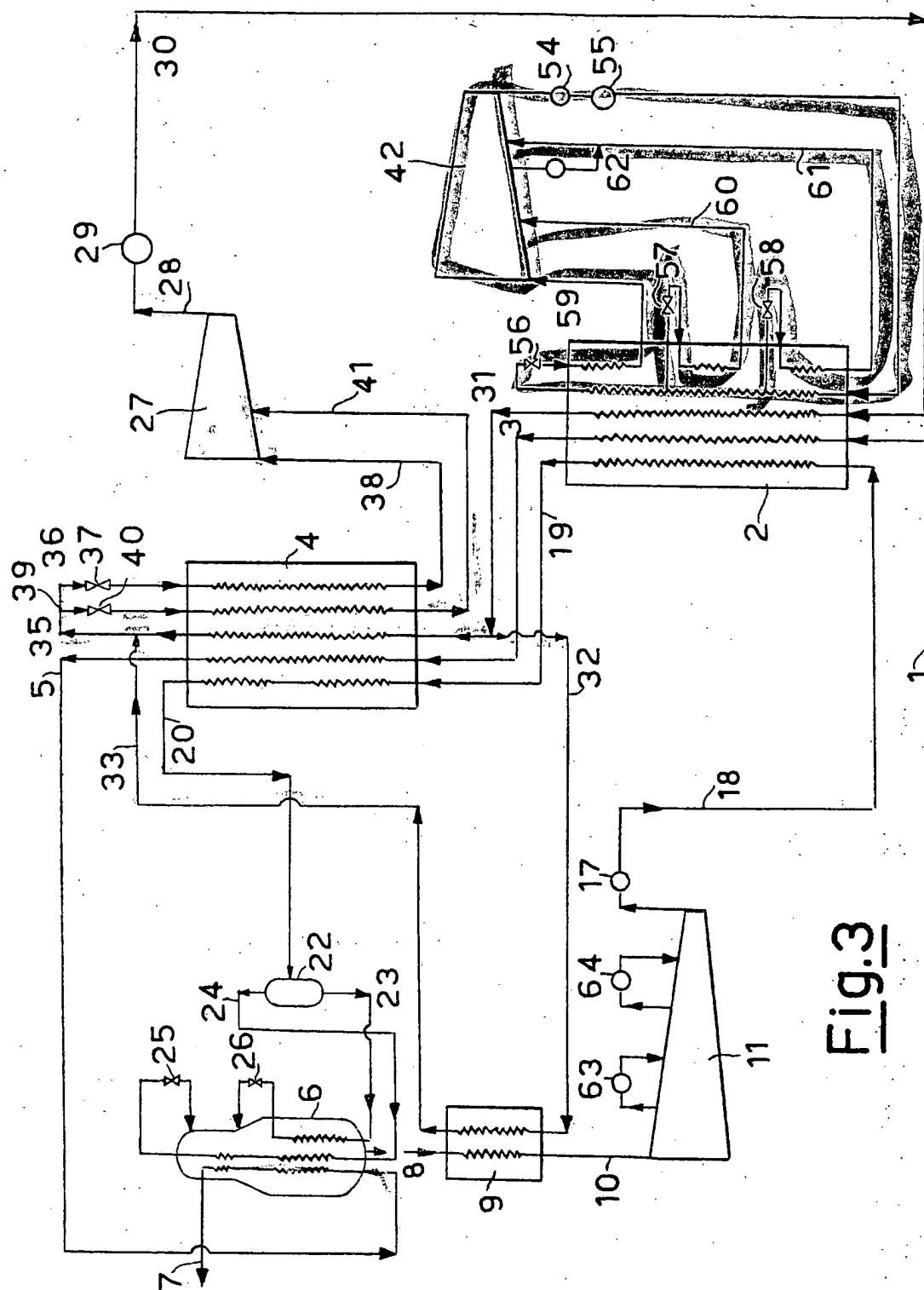


Fig. 3

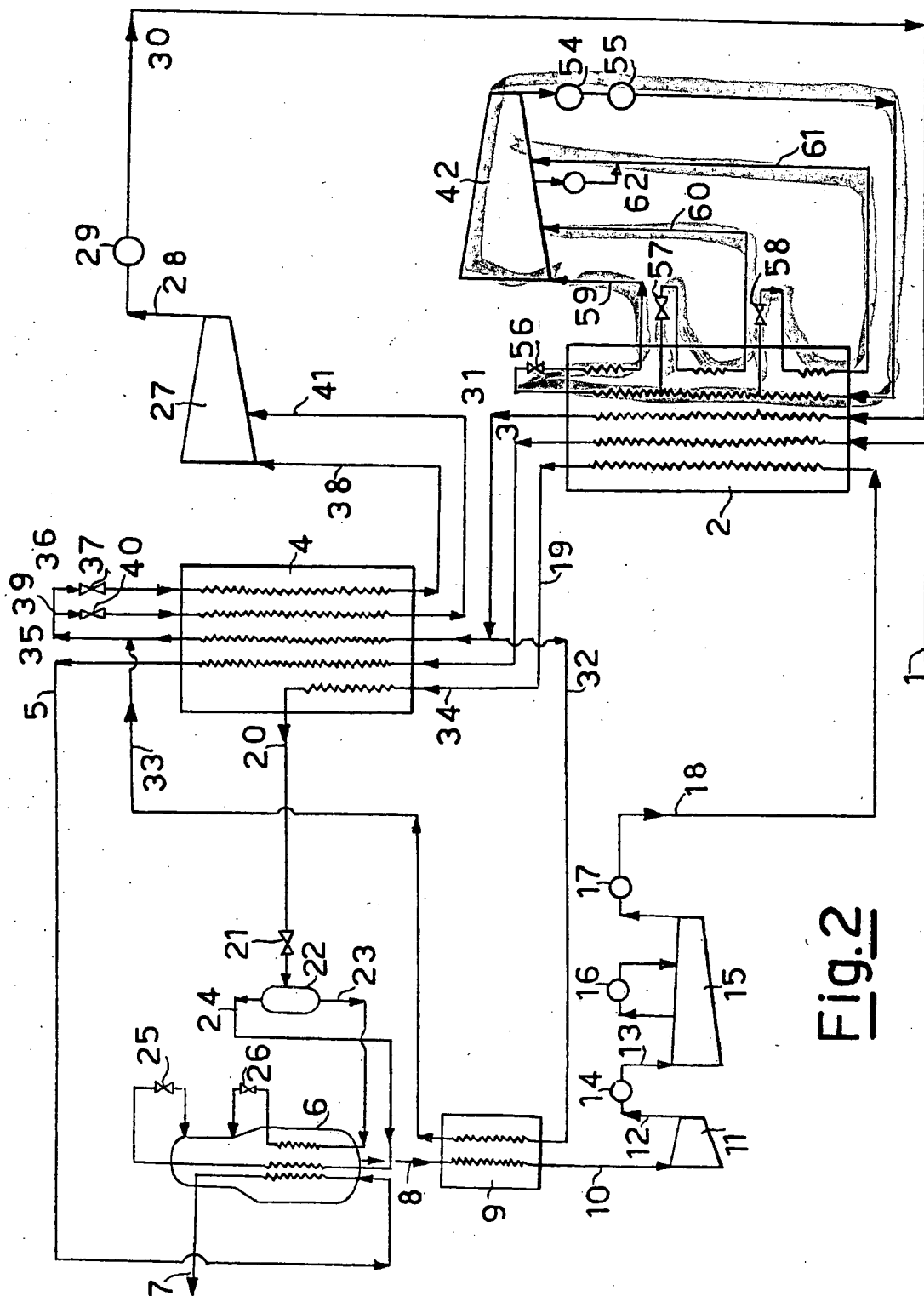


Fig.2







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